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Photo-assisted molecular engineering in solution-processed organic thin-film transistors with a blended semiconductor for high mobility anisotropy

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This paper reports a viable method for enhancing mobility anisotropy in solution-processed organic thin-film transistors (TFTs) by irradiating linearly polarized ultraviolet (LPUV) light onto a 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene)/poly (vinyl cinnamate) (PVCi) blended semiconductor film. The needle-like crystalline domains in the blended semiconductor film were aligned along the polarization direction of the LPUV light, suggesting that TIPS-pentacene molecules are oriented anisotropically due to an intermolecular interaction and aggregation with the photo-aligned PVCi molecules. The mobility anisotropy reached up to about 50, which is the highest value achieved in solution-processed organic TFTs with a polymeric insulator. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4774001]

Organic thin-film transistors (TFTs) have attracted considerable attention for potential applications, such as active-matrix flexible displays, electronic identification cards, and various optoelectronics devices due to the low-cost, low-temperature, and large-area processability.[1,2] Most research on organic TFTs has focused on enhancing device performance and understanding the fundamental physics related to TFT operation.[3,4] Recently, the field-effect mobility of these TFTs, which is one of the most important parameters needed to evaluate the TFT characteristics, became comparable to or even better than that of the amorphous silicon TFTs currently used as the switching element in flat-panel displays.[5] Although the mobility in organic TFTs appears to be sufficient for practical applications, several critical issues still need to be addressed. In particular, to promote their implementation into commercial electronic devices, the degree of cross-talk in the TFT backplane, which is caused mainly by undesirable current flow between the adjacent pixels, should be considered when organic TFTs are used in large-scale integrated circuits.[6,7]

For TFTs fabricated from vacuum-deposited organic semiconductors, it was reported that the cross-talk features can be suppressed by introducing an alignment layer on the gate insulator that contributes to the anisotropic growth of the thermally evaporated organic molecules. For example, physical rubbing[8,9] or photo-aligning techniques,[10] which are generally used to align liquid crystal (LC) molecules, have been evaluated as methods to produce aligned organic semiconductor films. Shang *et al*. reported a mobility anisotropy greater than 15 for small molecule-based organic TFTs with an inorganic insulator.[11] Similarly, in cases of solution-processed organic semiconductors, several approaches have been made to minimize cross-talk by patterning and/or aligning solution-processed organic semiconductor molecules. This can be achieved directly by patterning organic semiconductor layers or indirectly by transferring patterned organic semiconductor layers.[12,13] Loo suggested that the selective patterning of solution-processed organic semiconductors using UV light helps reduce electrical cross-talk between neighboring devices.[14] On the other hand, such patterning techniques for solution-processed organic semiconductors are still challenging because of the undesirable degradation in organic semiconductor films during the patterning process. Alternatively, many researchers have turned their attention to inducing mobility anisotropy by directly aligning the solution-processed organic molecules. For example, several approaches have been explored, such as tilting of the substrate, modification of the interface, and controlling solvent evaporation.[15–18] Although these approaches can enhance the molecular orientation in the film, they still involve uncontrollable and complex processes. This letter proposes a simple and viable way of obtaining high anisotropic electrical properties in solution-processed organic TFTs for minimizing cross-talk through photo-assisted molecular alignment in an engineered organic semiconductor film.

Figure 1 shows a schematic diagram of the organic TFTs and corresponding chemical structures of the organic semiconductor, 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene) and photo-reactive polymer, poly(vinyl

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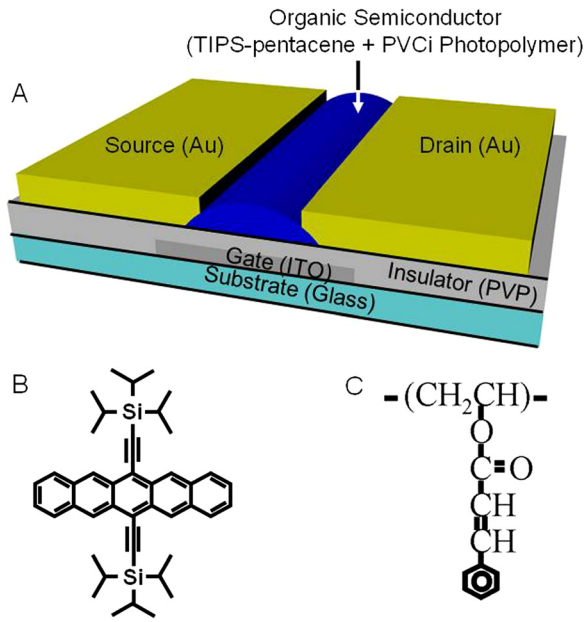

FIG. 1. (a) Schematic diagram of the organic TFTs with a solution-processed polymeric insulator, PVP. Chemical structures of the soluble organic semiconductor, TIPS-pentacene, and the photo-reactive polymer, PVCi are shown in (b) and (c).

cinnamate) (PVCi). As a gate insulator, poly(4-vinylphenol) (PVP) (Mw = 20 000 g/mol) was used mixed with 125 wt. % methylated poly(melamine-co-formaldehyde) (MMF) as a cross-linker.[19] The PVP with MMF was dissolved in propylene glycol methyl ether acetate in 10 wt. %. The solution was spin-coated at 3000 rpm for 30 s, and cured at 100 °C for 1 min and 200 °C for 5 min for thermal cross-linking. The film thickness and capacitance per unit area were approximately 550 nm and 6.3 nF/cm^2, respectively. As an active layer, TIPS-pentacene and PVCi (1:1) were dissolved in 1,2-dichlorobenzene. The blended solution was drop-casted on top of the cross-linked PVP insulator and cured at 60 °C for 5 min with or without exposing the film to linearly polarized ultraviolet (LPUV) light, which was generated from a Xe-Hg lamp with a power of 9 mW/cm^2. The 80 nm-thick-Au source and drain electrodes were evaporated thermally onto the blended active layer at a rate of 1.0 Å/s. The channel length (L) and width (W) were 100 μm and 1000 μm, respectively. The current-voltage characteristics were measured using a semiconductor parameter analyzer (HP 4155A) at room temperature under ambient pressure.

Figure 2 shows the optical microscopy images of the TIPS-pentacene/PVCi blended films. The blended film clearly shows some degree of directional orientation corresponding to the direction of the LPUV light exposure during the solvent curing steps. Under no UV light exposure, the blended film showed a radial shape, which means that the TIPS-pentacene molecules were distributed randomly (Fig. 2(a)). On the other hand, in the cases of LPUV light exposure, the needle-like crystalline domains were aligned approximately parallel to the LPUV direction shown in Figs. 2(b) and 2(c). Therefore, it was assumed that TIPS-pentacene molecules in the present blended films can be aligned by exposure to LPUV light.

The polarized UV-/vis. absorption spectra of the LPUV-exposed TIPS-pentacene/PVCi blended film revealed the

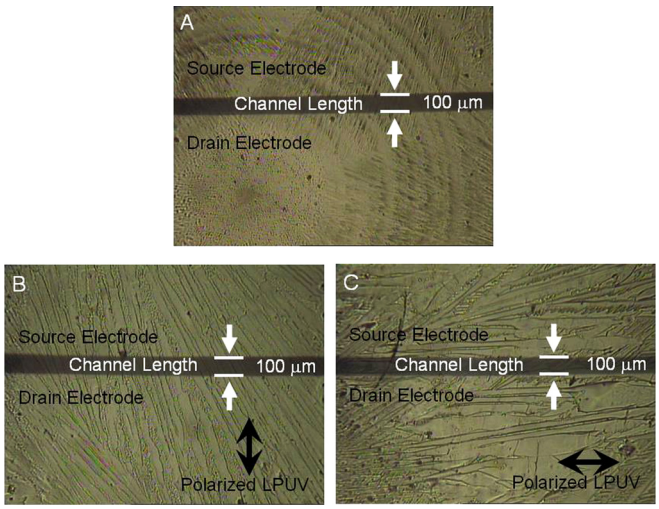

FIG. 2. Optical microscopy images of the TIPS-pentacene/PVCi blended films for (a) non-polarized UV light exposure, (b) parallel directed LPUV light to the carrier flow, and (c) perpendicular directed LPUV light to the carrier flow.

anisotropic arrangement of the TIPS-pentacene molecules in the blended film. In Fig. 3, the blended film showed a notable difference in the UV-/vis. absorption spectra according to the polarization direction of the light source. The UV-vis. absorption in the TIPS-pentacene/PVCi blended film was considerably intense when the UV-vis. light was polarized parallel to the LPUV direction. This suggests that the TIPS-pentacene molecules are oriented structurally along the direction of the LPUV, which also explains the directional growth of the crystalline domains shown in Fig. 2. Note that a dichroic ratio in the UV-/vis. absorption spectra is generally used to evaluate the molecular orientations in organic semiconductor films.[20] The difference in the absorption intensity of the TIPS-pentacene/PVCi blended film can be attributed to the anisotropic arrangement of the TIPS-pentacene molecules. This is because the absorption intensity of the TIPS-pentacene under the parallel exposed LPUV

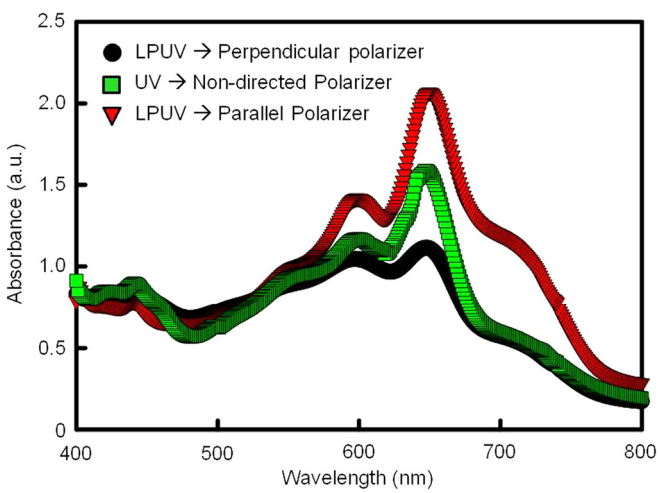

FIG. 3. Polarized UV-/vis. optical absorption spectra for the three cases. The circles and reverse triangles represent the different directions of the linear polarizer to the direction of the LPUV light exposure during solvent curing. The squares represent the case of non-directed polarizer-used measurements.

case was higher than that of the non-polarized UV case and the power of LPUV light was significantly lower than the non-polarized UV light. It is known that the photo-reactive cinnamate groups in PVCi films dissociate as a consequence of the adsorption of the parallel polarized UV light, which results in structural anisotropy in the PVCi film.[21] In other words, the LPUV light illumination causes an anisotropic deletion of the cinnamoyl side chains in the PVCi molecules.[22] For the mixed film, the photoreactions are likely to be affected by several properties, such as intermolecular interactions, degree of aggregation, and the π-π stacking of the TIPS-pentacene molecules. The anisotropic PVCi molecules can give rise to anisotropic interactions with the TIPS-pentacene molecules, along with the self-aggregation strength via a molecular interaction at the covalent bond of the carbon atoms. Based on our observations of the polarized UV-/vis. absorption spectra in the TIPS-pentacene/PVCi blended film, we deduced that the side chains of the TIPS-pentacene molecule tend to be oriented perpendicular to the cinnamoyl side chains of PVCi in the LPUV-exposed blended film and thus the main chain of TIPS-pentacene aligns along the polarization direction of UV light. It should be also noted that pentacene molecules which resemble the main chain of TIPS-pentacene in a chemical structure are not aligned on the LPUV-exposed PVCi film.[4] It implies that the interaction between the side chains of the TIPS-pentacene and the cinnamoyl side chains of PVCi predominantly induces the arrangement of the TIPS-pentacene molecules in the blended film. Accordingly, we consider that the needle-like domains in the blended film can be directionally aligned as a consequence of the anisotropic arrangement of the TIPS-pentacene molecules, which would be formed parallel to the polarization direction of the UV light. Recently, Cho *et al.* reported the effect of the segregation strength or degree of phase separation for an isotropic polymer/TIPS-pentacene blended film on device performance using the Flory-Huggins theory.[23] Nevertheless, the present study focused on the aligned features of the TIPS-pentacene/PVCi blended film after exposure to LPUV light.

The effects of the anisotropically aligned TIPS-pentacene molecules in the organic TFTs on the electrical properties were now examined. Three different types of organic TFTs were fabricated to determine the degree of mobility anisotropy. Type 1 was a TFT with randomly oriented TIPS-pentacene molecules, which was fabricated without exposure to LPUV light. For Type 2, LPUV light was irradiated parallel to the direction for charge conduction in the channel of the transistor. The TIPS-pentacene molecules were oriented parallel to the charge-transport direction. Finally, for Type 3, the blended film was irradiated with LPUV light in the direction perpendicular to the conduction channel in the TFT. Figs. 4(a)–4(c) present the output characteristic curves of three different types of organic TFTs, respectively. For each case, the magnitude of the drain current for -40 V at both the gate voltage and drain voltage was approximately $-2\,\mu$A (Type 1), $-10\,\mu$A (Type 2), and $-0.25\,\mu$A (Type 3). As expected from the TIPS-pentacene distribution from the optical image and UV-/vis. absorption spectrum, the parallel-exposed LPUV case showed the highest current, possibly due to the parallel-aligned TIPS-pentacene molecules along the carrier flow direction.

From the transfer characteristic curves in Fig. 4(d), the mobility in the saturation region was calculated using the following equation:

$$\mu = 2 \cdot \frac{L}{W} \cdot \frac{1}{C_i} \cdot \frac{I_D}{(V_G - V_T)^2},$$

where μ is the mobility, C_i is the capacitance of the gate insulator, I_D is the drain current, V_G is the gate voltage, and V_T is the threshold voltage. The mobility values reported were the maximum obtained from six different samples. At a fixed drain and gate voltage of -40 V, the mobility μ for Types 1, 2, and 3 was 0.046 cm^2/Vs, 0.382 cm^2/Vs and 0.008 cm^2/Vs

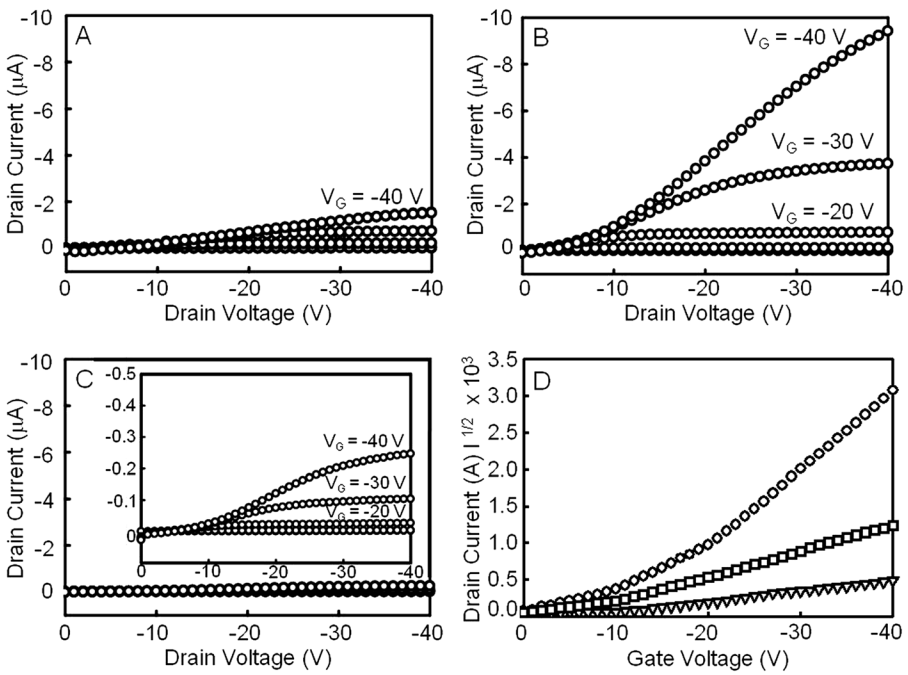

FIG. 4. Output characteristic curves of TIPS-pentacene/PVCi blened organic TFTs with (a) non-polarized UV light exposure, (b) parallel LPUV exposure to the direction of the carrier flow, and (c) perpendicular LPUV exposure to the direction of the carrier flow. The inset in (c) shows enlarged current-voltage characteristics. (d) Corresponding transfer characteristic curves at a drain voltage of -40 V. The dashed line, solid line, and the dashed-dotted line represent the non-polarized UV light case of (a), parallel directed LPUV exposure case of (b), and perpendicular directed LPUV exposure case of (c).

TABLE I. Comparison of the mobility anisotropy in an OTFT. $\mu_{\|}$ and $\mu_{\perp}$ represent the mobility parallel to and perpendicular to the surface treatment direction, respectively.

	Organic semiconductor	Film formation	Gate insulator	Technique	$\mu_{\|}$ [cm^2/Vs]	$\mu_{\perp}$ [cm^2/Vs]	Mobility anisotropy[a]
Our work	TIPS-pentacene	Solution-process	PVP	Photo-alignment	0.382	0.008	47.8
Ref. 17	TIPS-pentacene	Solution-process	PVCi	Photo-alignment	0.12	0.06	2.0
Ref. 16	F8T2	Solution-process	PI/SiO_2	Rubbing	4×10^{-3}	1×10^{-3}	4.0
Ref. 15	TIPS-pentacene	Solution-process	SiO_2	Controlled deposition	0.02	0.16	8.0
Ref. 10	Pentacene	Vacuum-deposition	Polymer/SiO_2	Photo-alignment	0.3	0.05	6.0
Ref. 3	Pentacene	Vacuum-deposition	Polymer/SiO_2	Photo-alignment	0.40-0.75	0.09-0.015	2.7-8.3
Ref. 8	Pentacene	Vacuum-deposition	PVA	Rubbing	0.008	0.02	2.5
Ref. 9	Pentacene	Vacuum-deposition	PVA/PVP	Rubbing	0.31	0.12	2.6
Ref. 11	CuPc	Vacuum-deposition	SiO_2	Etching	0.001	0.016	16.0

[a]Mobility anisotropy was determined from the ratio between $\mu_{\|}$ and $\mu_{\perp}$.

flow, respectively. In contrast, the mobility of the TIPS-pentacene only case (no blending) was 0.185 cm^2/Vs. Under the given processing conditions, the calculated mobility for the six different samples were consistent within a mean deviation of $\pm 4\%$. The magnitude of the mobility for all these cases could be improved more after optimizing the fabrication processes, such as the mixing ratio between the polymeric polymer and TIPS-pentacene and purification of the materials. However, the main aim of this study was to determine a scalable way of controlling the crystal orientation and resulting anisotropic mobility features. The anisotropic mobility between the parallel LPUV exposure case and perpendicular LPUV exposure case in the blended organic semiconductor used TFTs was as high as around 50. This value is the highest for solution-processed organic TFTs with a polymeric insulator. The comparative analysis between our work and previous studies in terms of the mobility anisotropy is specifically summarized in Table I. Furthermore, it is worth noting that the increased ratio of the mobility between the TIPS-pentacene only case and the blended TIPS-pentacene case (parallel LPUV exposure case) is about 2. This means that the blending of organic semiconductors and polymers would be a good way of achieving improved electrical properties as well as obtaining high anisotropic values, which is essential for minimizing the cross-talk phenomena. Since the charge transport in organic semiconductors is influenced predominantly by π orbital overlap between molecules, the charges transport preferentially along the stacking axis of the organic semiconductor molecules through overlapped π orbitals induced by the alignment of molecules. Hence, mobility anisotropy can be achieved.

In summary, this paper presents an effective and easy way of achieving high mobility anisotropy as well as improving the mobility in solution-processed blended organic TFTs with a polymeric insulator. When LPUV light was exposed to the blended film, TIPS-pentacene molecules in the blended film were found to be aligned along the direction parallel to the LPUV light due to self-segregation and intermolecular interactions between the TIPS-pentacene and photo-polymer; PVCi films were effectively aligned by exposure to LPUV light. For TIPS-pentacene aligned along the direction of the crystalline domains, the anisotropic mobility reached approximately 50, which is the highest value in a solution-processed organic TFT with a polymeric insulator. Based on this approach, it is possible to provide a platform for developing solution-processed electronic integrated circuits with minimal cross-talk and improved electrical properties. Nevertheless, more studies will be needed to better understand the physical mechanism of how the organic semiconductor molecules are affected by the photo-reactive photo-polymers in the blended case.

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